

INCREMENTAL IDENTIFICATION OF A FULL MODEL OF A TWO-PHASE FRIEDEL-CRAFTS ACYLATION REACTION

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Summary

Due to the efficient product separation and catalyst immobilization, multi-phase catalytic systems are attractive for industrial applications. Nevertheless, it is usually difficult to decouple reaction and mass transfer kinetics such that the experimental determination of reaction kinetics is masked by mass transfer effects. A novel incremental identification methodology tailored to homogeneous reaction systems and extended to multi-phase systems in previous works allows for the decoupling of reaction kinetics and mass transfer and thus avoids the uncertainty in reaction kinetics identification by construction. While the method has been demonstrated in a simulation case study before, it is applied in a real experimental study of a multiphase system thoroughly for the first time.

Keywords

Two-phase reaction system, incremental model identification, optimal design of experiments, model structure discrimination

Introduction

Obtaining exact process models in chemical industry is an important task. As a first step in model identification, the underlying phenomena determining the behavior of the reaction system should be examined. This is especially difficult in case of reactive fluid multiphase systems which are attractive due to their efficiency in catalyst immobilization and product separation [1]. The difficulty arises from the coupling of reaction and mass transfer phenomena in such systems.

Novel incremental model identification methodologies, developed at AVT, RWTH Aachen University [2] and at Laboratoire d'Automatique, EPFL [4], allow for the decoupling of reaction and mass transfer kinetics and hence enable to reliably identify a full model following the steps of a model development. Both methodologies, tailored to multi-phase systems in previous works, avoid the uncertainty in reaction kinetics identification by design. While the methods have already been validated in simulated case studies [2], [4], one of them, i.e. the one reported in [2] and currently under experimental investigation [3], is applied to a multi-phase system.

The current study comprises an isothermal Friedel-Crafts acylation of anisole in an ionic liquid with n-heptane used as a non-reactive second phase. The mechanism is rather complex and constitutes of three micro-reactions: in the first two steps, the reactants anisole and acetic anhydride first bind to the immobilized lanthanide triflate catalyst and then spontaneous reaction and product release (MAP and acetic acid) occurs.

Methodology

As a first step in model identification, the mass balances of all components in both phases are constructed without specifying rate laws for neither reaction nor mass transfer kinetics. The reaction and mass transfer rates are determined as a function of time from measured concentrations by differentiation. Since differentiation of noisy experimental data will amplify the noise level in the estimated rates, special care has to be taken. In particular, smoothing splines and Tikhonov regularization with generalized cross validation for regularization parameter selection have been used to calculate the reaction and mass transfer rates from the mass balances.

In the next step, the two-phase reaction model is

reformulated into a pseudo-single phase system. The stoichiometric matrix is constructed accordingly. The rows of the constructed pseudo-stoichiometric matrix are pseudo-rates, where the first row represents the reaction and the others represent mass transfer. The columns, on the other hand, represent the component coefficients for the corresponding rate phenomenon in the n-heptane and ionic liquid phases, respectively. Using the stoichiometric matrix, a rate expression matrix can be calculated as shown in [2].

After identification of the rates, several model candidates for reaction and mass transfer rates are tested using algebraic regression to identify sound estimates for the reaction rate constants in the reaction rate expressions and for the mass transfer coefficients in the mass transfer models.

After an initial analysis of experimental data, discrimination of model candidates can be performed on the basis of the associated Akaike Information Criterion (AIC) values. The AIC expression, first introduced by Akaike in the 1970s [5], constitutes a likelihood function which can rank the model candidates based on how good they can represent the measurement data. This can lead to a criterion for designing optimal experiments in order to increase the difference between the AIC values of model candidates for better discrimination [5]. The degrees of freedom for designing optimal experiments are initial concentrations of all components in both phases.

Model structure identification has been based on several reaction rate model candidates. Both elementary reaction rate expressions and complex ones, typically encountered in enzymatic bio-reactions, were considered. Reversibility was also taken into account. There are also a couple of empirical reaction rate expressions suggested in the literature which were considered [6], [7]. Those expressions take product inhibition phenomenon into account.

Model structure identification of mass transfer laws has been based on simple mass transfer rate expressions as well as on more complex ones accounting for diffusional cross effects [8].

The experimental set-up of the case study comprises of a stirred batch reactor which is operated isothermally. A full phase separation is ensured by rigorous stirring and an appropriate control of the liquid-liquid interface. ATR-IR spectroscopy has been used for measurement of all components in both phases.

Results and Outlook

Initial results of reaction rate expression model identification indicate that empirical models fit the experimental data best. After conducting optimal experimental designs for model discrimination as sketched above, the reaction rate candidate with

exponential product inhibition turned out as the best. This optimal design not only allowed for better discrimination but also increased the parameter confidence and reduced the correlation between parameters. Further analysis will be conducted on a more deliberate investigation of the reaction mechanism which surely does not account for the best fitting model candidate.

Mass transfer rate analysis showed that diffusional cross effects considered initially due to the complex behavior of the system indeed take place. Moreover, different types of cross effects are observed; thus, model candidates of different complexity are formulated and tested. A more rigorous analysis is in progress to improve the robustness of the mass transfer model and hence the overall reaction system model.

Usage of activities instead of concentrations is also under investigation. Since the system in consideration is a highly complex, we believe this issue is worth tackling.

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Incremental model identification of reaction and mass transfer kinetics in a liquid-liquid reaction system – An experimental study

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Due to the efficient product separation and catalyst immobilization, multi-phase catalytic systems are favoured in industrial applications [1]. Nevertheless, it is usually difficult to decouple reaction and mass transfer kinetics such that the experimental determination of reaction kinetics is masked by mass transfer effects. A novel incremental identification methodology tailored to homogeneous reaction systems [2] and extended to multi-phase systems in previous works [3] allows for the decoupling of reaction kinetics and mass transfer and thus avoids the uncertainty in reaction kinetics identification by construction. While the method has been demonstrated in a simulation case study before [3] it is applied in a real experimental study of a multiphase system for the first time in this work.

The chemical system studied comprises a Friedel Crafts acylation of anisole. It follows a complex reaction mechanism with two reactants and two products on the surface of the catalyst. Several reaction rate models, both elementary and complex, were analyzed. The quality of the candidate models has been assessed by the residual sum of squares (RSOS) serving as an objective function and the Akaike Information Criterion (AIC). Optimal experiments were designed to improve model quality using a novel AWDC criterion [4]. It was found out that a reaction rate model comprising only two rate constants for the forward and backward reactions respectively fits the best with a small confidence interval in contrast to the suggested mechanism in literature [5].

Since mass transfer and chemical reaction can be systematically decoupled in the identification procedure, the best fitting mass transfer rate model of the 4 species involved can also be determined from the same experimental data set. Several mass transfer models of increasing complexity [6] were tested. Our preliminary results show that a simple model which neglects the diffusion cross effect fits the experimental data best. An optimal design of experiments will be conducted next to improve the reliability of the mass transfer model.

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Incremental Model Identification of Reaction and Mass Transfer Models of a Two-Phase Friedel-Crafts Acylation Reaction System

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Introduction

Obtaining exact process models in chemical industry is an important task. As a first step in model identification, the underlying phenomena determining the behaviour of the reaction system should be examined. The difficulty arises from the coupling of reaction and mass transfer phenomena in such systems. Novel incremental model identification methodologies, developed at AVT, RWTH Aachen University [2] and at Laboratoire d'Automatique, EPFL [4], allow for the decoupling of reaction and mass transfer kinetics and hence enable to reliably identify a full model following the steps of a model development. While the methods have already been validated in simulated case studies [2], [4], one of them, i.e. the one reported in [2] and currently under experimental investigation [3], is applied to a system comprising a Friedel-Crafts acylation of anisole in an ionic liquid with n-heptane used as a non-reactive second phase.

Methodology

As a first step in model identification, the mass balances of all components in both phases are constructed without specifying rate laws for neither reaction nor mass

transfer kinetics. In the next step, the two-phase reaction model is reformulated into a pseudo-single phase system. The stoichiometric matrix is constructed accordingly. Using the stoichiometric matrix, a rate expression matrix can be calculated [2]. Model structure identification has been based on several reaction rate model candidates. Both elementary reaction rate expressions and complex ones, typically encountered in enzymatic bio-reactions, were considered. Empirical models were also taken into account [5], [6]. Model structure identification of mass transfer laws has been based on simple mass transfer rate expressions as well as on more complex ones accounting for diffusion cross effects [7]. The experimental set-up of the case study comprises of a stirred batch reactor which is operated isothermally. A full phase separation is ensured by rigorous stirring and an appropriate control of the liquid-liquid interface. ATR-IR spectroscopy has been used for measurement of all components in both phases.

Results and Outlook

Initial results of reaction rate expression model identification indicate that empirical models fit the experimental data best. After conducting optimal experimental designs for model discrimination, the reaction rate candidate with exponential product inhibition turned out as the best. Mass transfer rate analysis showed that diffusion cross effects considered initially due to the complex behaviour of the system indeed take place. The full model of the system is going to be constructed next.

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